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Summary Report on Corrosivity Studies in Coincineration of Sewage Sludge and Solid Waste

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SUMMARY REPORT ON CORROSIVITY STUDIES IN COINCINERATION OF SEWAGE SLUDGE AND SOLID WASTE

by

H.H. Krause, P.W. Cover, and W.E. Berry
Battelle's Columbus Laboratories
Columbus, Ohio 43201

Grant No. R804008-02-2

Project Officers

Michael I. Back
and
Robert A. Olexsey
Hazardous Waste Engineering Laboratory
Thermal Destruction Branch
Cincinnati, Ohio 45268

HAZARDOUS WASTE ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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16. ABSTRACT

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

The subject of this report is an evaluation of the effects of combustion solid waste with sewage sludge in a municipal incinerator. The information contained herein will be of interest to those involved in the purchase, design, construction, or operation of waste-to-energy systems.

For further information, please contact the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory.

David G. Stephan, Director
Hazardous Waste Engineering Research Laboratory

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ABSTRACT

Corrosion probe exposures were conducted in the Harrisburg, Pennsylvania Incinerator to determine the effects of burning low-chloride sewage sludge with municipal refuse. Probes having controlled temperature gradients were used to measure corrosion rates for exposure times up to 816 hours. The effects of exposure time, metal temperature, and gas temperature were studied. The results demonstrated that the addition of the sludge reduced the initial corrosion rates of carbon and low-alloy steels to about half of that from refuse alone. Little effect was observed on the rates for Types 310 and 347 stainless steels. An aluminized coating on steel resisted corrosion effectively and offers promise as a cost-effective substitute for expensive alloys. In the range 260–482°C (500–900°F), corrosion rates were significantly reduced and were less dependent on metal temperature. The addition of sludge to refuse is recommended as a corrosion prevention measure and a waste disposal technique.

This report was submitted in fulfillment of Grant No. R804008-02-2 by the Columbus Laboratories of Battelle Memorial Institute under the sponsorship of the U.S. Environmental Protection Agency. This work was conducted during the period November 1, 1977 and November 30, 1978.

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SECTION 1

INTRODUCTION

Corrosion of boiler tubes has been a significant problem for waterwall incinerators in which bulk refuse is burned, particularly if superheated steam is generated. During the initial operation of the Harrisburg, Pennsylvania Incinerator, when only bulk solid waste was burned, tube failures occurred every three to five months. However, for the past two and a half years no tube failures have occurred, but during this period municipal sewage sludge has been burned along with the solid waste. In addition, soot blowing was reduced in frequency and some of the carbon steel tubes were replaced with a low chromium alloy. Consequently, the reason for the reduced metal wastage at the Harrisburg Incinerator was uncertain and corrosivity studies were needed to evaluate the effect of adding the sewage sludge to the refuse combustion environment.

As currently practiced, the dewatered sludge filter cake containing about 22 percent solids is mixed with the municipal refuse in the receiving pit. Considerable mixing occurs in the pit before the sludge and refuse are fed into the furnace charging chute. The weight ratio of sludge to solid waste is about 1 to 10 on an as-received basis, and it seemed likely that the sulfur and silica in the sewage sludge are present in sufficient quantity and are burned effectively to overcome the corrosive effects of chlorine in the refuse.

The objective of this research program was to determine the effect of the addition of low chloride sewage sludge to municipal solid waste on the wastage rates of boiler tube metals. Both short- and long-term wastage was measured during this program.

SECTION 2

CONCLUSIONS

Corrosion probe exposures conducted at the Harrisburg, Pennsylvania, Incinerator demonstrated that the addition of low-chloride sewage sludge to municipal refuse reduced the corrosion of susceptible metals caused by chlorine in the refuse. Specific conclusions from this research program were:

(1) The corrosiveness of the refuse combustion environment to carbon steel as indicated by 8-hour exposures was only one half as great with sewage sludge present. Less reduction occurred with T22 steel, although the corrosion rate with sludge was the same as that for carbon steel. Very little reduction occurred with Incoloy 825 and essentially none with Types 310 and 347 stainless steel, which have very low corrosion rates with refuse alone.

(2) The corrosion resistance of alloys to the refuse-sludge combination in decreasing order was Incoloy 825; 310 stainless steel; 347 stainless steel; T22 low chromium alloy; and A106 carbon steel. A diffusion-bonded aluminum coating on steel remained intact during the exposures and could be a cost-effective alternative.

(3) The corrosion rates decreased with exposure time in the presence of sewage sludge and appeared to level off at about 1000 hours.

(4) For carbon and low alloy steels the corrosion rates increased with metal temperature in the range 260–482°C (500–900°F), while those for stainless steel decreased.

(5) The short-term corrosion rates at gas temperatures of 593–649°C (1100–1200°F) were only one-fifth as great as at 815°C (1500°F) and showed less increase with metal temperature.

(6) The increased superheater tube life at the Harrisburg Incinerator is the result of (1) addition of sewage sludge, which contributes large amounts of SiO_2 to the combustion environment, (2) reduced frequency of soot blowing, leaving protective oxidation products on the metal, and (3) use of T22 alloy tubing, which showed greater resistance to corrosion than carbon steel when the refuse was burned without sludge.

SECTION 3

RECOMMENDATIONS

As a result of this research program it is recommended that cofiring of sewage sludge with municipal refuse be encouraged as a means of reducing corrosion of heat recovery surfaces and at the same time providing sludge disposal. However, it should be pointed out that the sewage should not have been treated with ferric chloride, because the chloride residue in the sludge would promote corrosion.

It also is recommended that boilers intended to burn refuse be designed so that gas temperatures in the superheater zone are as low as possible. In this way higher superheater metal temperatures can be used with little increase in corrosion. The design should also provide combustion air in a manner that will minimize carbon monoxide formation near tube metal surfaces.

The corrosion resistance of aluminized coatings on carbon steel to the refuse combustion environment should be investigated more extensively. This type of coating offers a less expensive alternative to high chromium-nickel alloys to obtain longer tube life in refuse burning.

The use of silica as an additive to combat corrosion from refuse burning should be investigated. The beneficial effect of the sewage sludge observed in this program can be attributed in part to the silica content, because the total sulfur in the system was not great enough to account for the corrosion reduction.

SECTION 4

BACKGROUND

Construction of the Harrisburg Incinerator was started on December 22, 1969, and it began operation in October, 1972. This facility has two identical boilers, each with a nominal capacity of 327 Mg/day (360 tons/day) of refuse. At this rate of 13.6 Mg (tons) of refuse per hour, the normal steam production is 42.0 Mg/hr (92,500 lb/hr) with a peak of 54.5 Mg (120,000 lb). Design values are also generally maintained for superheater steam quality of 18.6 kg/cm^2 (250 psig) outlet pressure at a temperature of 236°C (456°F). These two multidrum boilers with welded waterwalls are fed from a single refuse pit and are exhausted through individual electrostatic precipitators before discharge into the single stack.

Figure 1 shows the location of the superheaters where the first tube failure occurred and where the corrosion probes were located for this study. Although Boiler Unit No. 1 started in operation (October 1972) before Unit No. 2, the shortest-lived superheater tube was in Unit No. 2 where a failure occurred after about 3000 hours. It failed with a ductile split several inches long while the wall thickness of adjacent tubes was reduced to 0.051 cm (0.020 inch) from their original 0.42 cm (0.165 inch) wall. Wall thickness of tubes remote from the soot blower was reduced to about 0.38 cm (0.150 inch).[1] By March 1974 the entire bank of carbon steel superheater tubes had been replaced with T22 alloy. Fortunately by this time the effect of soot blowing on metal wastage had been recognized and the blowers were used sparingly. Then in June 1975 the burning of sewage sludge with the refuse was begun, and this mode of operation has continued to the present.

Prior to delivery to the incinerator the sludge is processed conventionally. Wastes from the entire city and some of the adjacent regions are treated first by grinding, grit removal and preliminary settling. Subsequently anaerobic digesters are used with a polymer treatment to thicken the supernatant liquid. The coagulant used in the sludge treatment process is an organic-based filter aid, employed at the rate of 12.3 kg (27 lb) per 4545 kg (10,000 lb) of dry solids. As this organic polymer is probably a combination of amines and acrylates, it is much more suitable for use in sludge to be incinerated than is ferric chloride, which was used previously.

About 13.6–18.2 Mg (15–20 tons) of partially dried sewage sludge are delivered by truck to the incinerator every 24 hours, and the sludge is dumped onto the refuse in the pit. This material contains 20–22 percent solids, so the incinerator handles the equivalent of about 4500–5500 kg (5–6 tons) per day of dry solids. During the course of these corrosion studies the partially dried sludge was delivered at an average rate of 15,000 kg (16.5 tons) per working day.

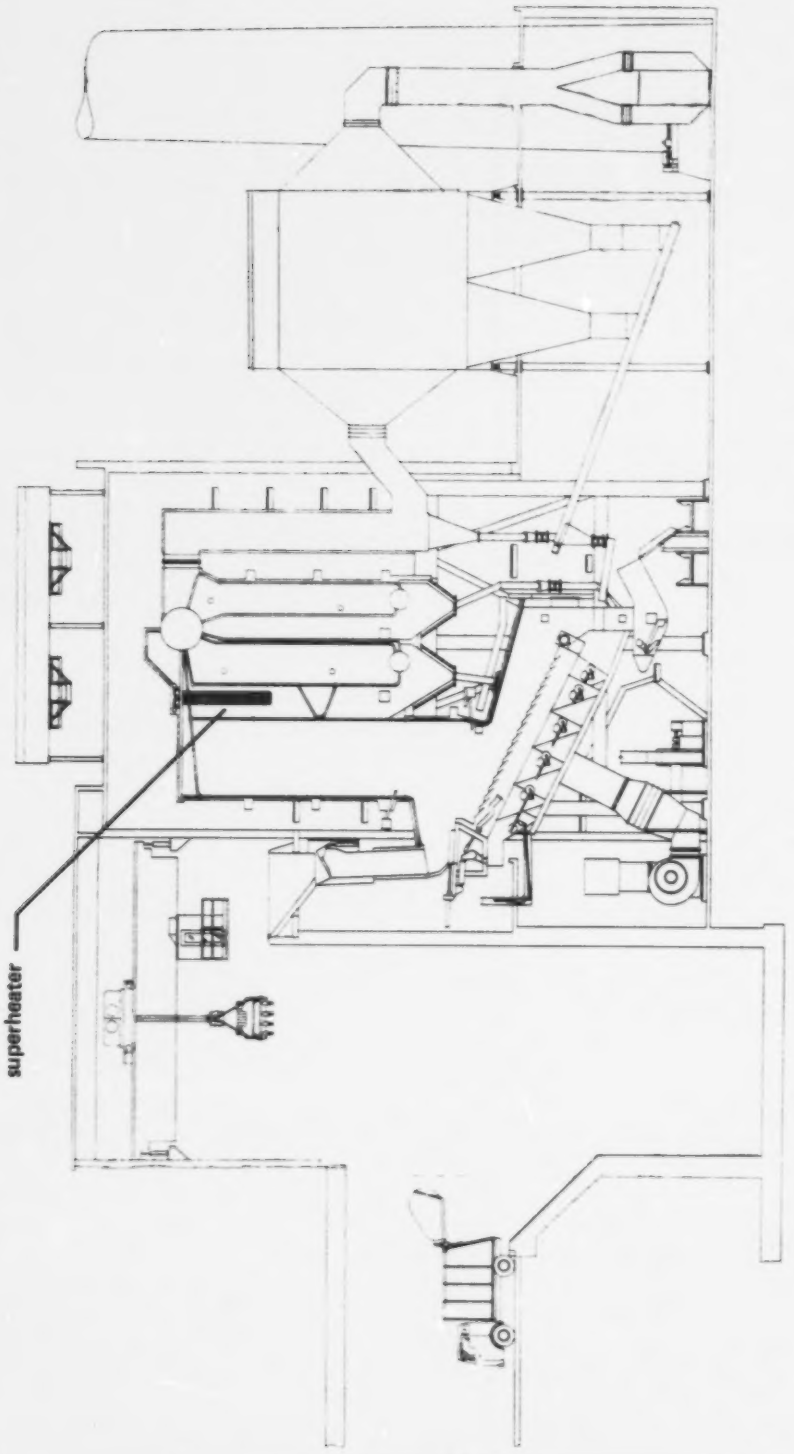

Figure 1. Harrisburg, Pennsylvania, refuse burning facility.

SECTION 5

FIRESIDE CORROSION STUDIES

During this program six corrosion probe exposures were made, with different exposure times, fuels, and gas temperatures. The conditions for these different corrosion-probe runs are shown in Table 1. During the 816-hour exposure an explosion and fire in the incinerator pit interrupted plant operations for about four weeks during which time the probe was removed and covered to protect it from damage. This interruption occurred after 100 hours' exposure and loss of protective deposits on several specimens resulted in slightly higher corrosion rates. One of the 8-hour probe exposures (No. 45) was interrupted briefly by a delay in sewage sludge delivery.

The sewage sludge was not delivered to the incinerator at uniform intervals in a 24-hour period. However, this timing was less critical in long-term experiments because the crane operators were able to extend the sludge distribution over the intervals between loads of sludge. The delivery and subsequent combustion of the sludge during the 800-hour exposure was somewhat irregular after the first week. However, as will be pointed out later, the early reactions at a clean metallic surface are the most important, and subsequent reaction of the deposit-encrusted tubes is less significant. Thus, short periods of operation on refuse alone after a protective oxide layer has built up on the tube have only a slight effect on the total corrosion that the metal will undergo.

FUEL EVALUATION

During this program no analyses were made of the refuse because this had been done extensively in the early days of operation of the Harrisburg Incinerator. No new sources of refuse of any importance had developed since that time, and visual inspection of the refuse pit during this program showed that typical municipal waste was being burned. The composition of the Harrisburg refuse as determined at the start-up period is shown in Table 2. The distribution of materials is typical of municipal refuse in the United States. The results of similar refuse classification at the Miami County Incinerator, Troy, Ohio are also presented in Table 2, because in this report corrosion probe data from that location are compared with the Harrisburg results. In general, the refuse compositions for the two sites are similar enough so that comparison of results is meaningful.

Samples of the wet sewage sludge as received at the Harrisburg Incinerator were taken on four different days during which probes were exposed. The samples were dried and analyzed for total sulfur and chlorine, heavy metals, and ash content. Only moderate drying conditions were used in order to avoid oxidation of the sludge. It was dried at a temperature of 50°C (120°F) for a month and then overnight at 110°C (230°F). The solids content of the sludge averaged about 20 percent. The heat of combustion of the sludge also was determined and was found to have an average value

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TABLE 1. CORROSION PROBE EXPERIMENTS AT THE HARRISBURG INCINERATOR

Probe No.	Exposure time, hours	Fuel	Location	Gas temperature, °C	Gas temperature, °F
41	8	Refuse	Superheater inlet	816	1500
42	8	Refuse	Superheater rear	621	1150
43	80	Refuse + sludge	Superheater inlet	816	1500
44	8	Refuse + sludge	Superheater rear	621	1150
45	8	Refuse + sludge	Superheater inlet	816	1500
46	816	Refuse + sludge	Superheater inlet	816	1500

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TABLE 2. REFUSE COMPOSITIONS

	Components, weight percent	
	Harrisburg, Pennsylvania[a]	Troy, Ohio[b]
Paper:		
Mixed	23.6	35.6
News	9.0	6.5
Corrugated	8.5	6.5
Magazines/books	2.3	3.2
Wood	2.6	3.6
Grass/garden waste	8.9	7.4
Cloth	3.3	2.1
Garbage, bones	5.1	10.3
Plastics:	–	4.0
Flexible	2.7	–
Rigid	1.0	–
Rubber	0.3	–
Miscellaneous fines	12.1	5.8
Dirt	9.8	–
Glass/ceramics	1.9	6.8
Metal:	–	8.2
Magnetic	7.6	–
Nonmagnetic	1.3	–

(a) Average of eight days in May 1972. (Ref. 1)
(b) Average of four days in 1972. (Ref. 2)

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of about 6960 J/g (3000 Btu/lb). This relatively low heating value supports the operator's experience that the sludge must be thoroughly distributed over the refuse in order to avoid quenching the flame in the incinerator.

During the 8- and 80-hour experiments, the sludge was delivered regularly with three loads a day totalling about 15,727 kg (17.3 tons). On the basis of a typical day's operation, the hourly consumption of wet sludge averaged about 659 kg (1450 lb) per hour together with about 27,090 kg (59,600 lb) of refuse between the two boilers at the incinerator. Assuming that half of this throughput went to each of the two boilers, Unit No. 1, in which the probes were exposed, produced very close to 1.4 kg (3 lb) of steam per 0.45 kg (1 lb) of fuel at the average observed steaming rate of 40,600 kg (89,300 lb) per hour. These refuse feed rates were based on the observation that there was an average of 827 crane loads per day charged into the two boilers. Measurements made at the beginning of operation of the incinerator in 1973 showed that the average weight of a crane load was 818 kg (1800 lb). Gross heating values for the normal refuse measured at the same time ranged from 9280 to 11,830 J/g (4000-5100 Btu/lb). The operational records of the incinerator showed a slight decrease in the steam conversion rate from the rate in 1973 of about 1.52 kg (3.35 lb) of steam per pound of refuse to about 1.41 kg (3.1 lb) of steam at the present time. This decline may be the result of reduced frequency of soot blowing. The high moisture content of the sludge which is burned in conjunction with the refuse also may be a contributing factor.

Analyses for total sulfur and for chloride made on the dried sludge gave an average value for sulfur of 3.4 percent, while the chlorides averaged 0.09 percent. In view of the small amount of sludge being burned, it could add only about 0.04 percent sulfur to the total fuel supply. Sulfur added to the system in this quantity would not be sufficient to counteract the corrosion due to the chlorine in the refuse. However, analyses of the sewage sludge and its ash by optical emission spectroscopy and X-ray diffraction showed that there is a high concentration of silica in both (Table 3). The combustion train yielded an average ash content of 68.1 percent with the major ingredient of the ash identified as silica (SiO_2). The SiO_2 content of the sludge is definitely higher than that of the municipal refuse. This material can function in the same manner as sulfur to inhibit corrosion by chlorine. In addition, the silica in the wet sludge is carried into the combustion zone, while in the case of the refuse alone the drier material allows the silica to sift out and be removed through the grates rather than to be carried into the hot combustion zone. As shown in Table 3, the other metals which were present in significant amounts were aluminum, calcium, iron, potassium, magnesium, and sodium.

EXPERIMENTAL APPARATUS AND PROCEDURE

The corrosion probe used in this program (Figure 2) was designed to include 18 cylindrical specimens nested together end-to-end and was then inserted into the superheater section of the boiler through a side wall. The section of the probe extending through the wall was water cooled. The specimens exposed within the furnace were cooled by air flowing inside the tubular specimens. A computer analysis was used to ascertain the geometry of the internal support tube required to give the most linear specimen-temperature variation over the range of about 177-510°C (350-950°F) for a probe with 18 specimens. Each specimen was about 1.25 inches in OD, 1.00 inch in ID, and 1.5 inches long. The specimens were nested together with lap joints as shown in Detail A and were retained axially at the cooling-air-outlet end by a retainer which was fixed to the internal support tube with webs as shown in Section A-A. The axial restraining force in the internal support tube

TABLE 3. ELEMENTAL ANALYSES OF DRY SEWAGE SLUDGE AND SLUDGE ASH

Element	Composition, weight percent	
	Sludge	Sludge ash
Si	10–20	20–40
Al	3–5	5–7
Ca	3–5	5–7
Fe	2–4	3–5
S[a]	3.35	4.9
K	0.8–2	1–4
Mg	0.5	0.8
Na	0.3	0.5
Ti	0.2	0.4
Cl[a]	0.09	0.13
Cu	0.08	0.2
Pb	0.08	0.1
Ba	0.05	0.1
Cr	0.06	0.1
Mn	0.05	0.08
Zr	0.01	0.03
Ni	0.01	0.02
Sn	0.01	0.02
V	<0.01	0.01
Co	<0.01	<0.01
Ag	<0.01	<0.01
B	<0.01	<0.01
Bi	<0.01	<0.01

(a) By wet chemistry; others by optical emission spectroscopy.

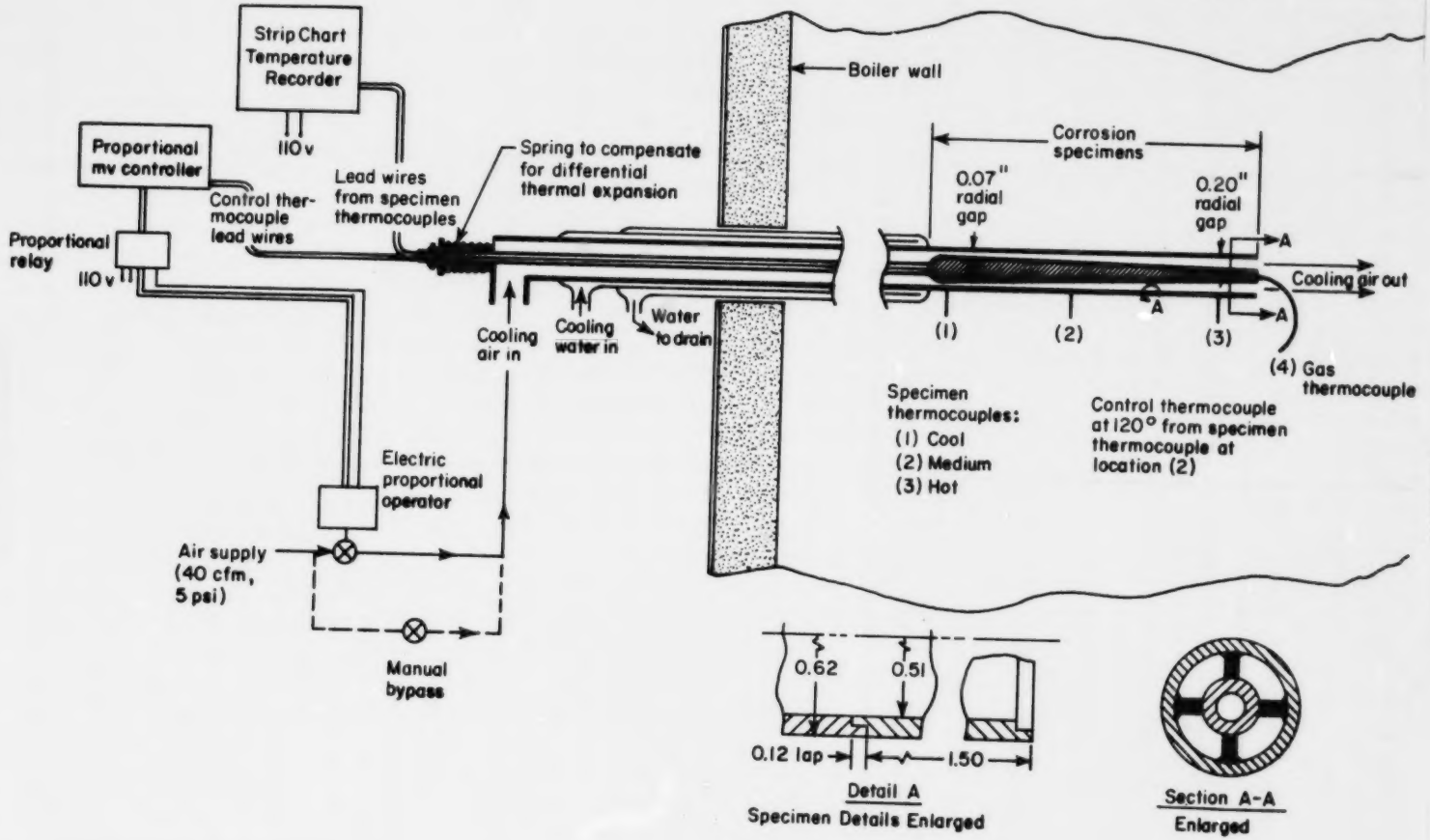

Figure 2. Schematic of specimen-exposure-probe apparatus.

was obtained by compressing the spring on the air-inlet end of the probe at assembly. Also, the spring compensates for differential thermal expansion between the specimens and the internal support tube.

Specimen temperatures were measured at three stations with Type K thermocouples (Chromel-Alumel) inserted into recesses drilled lengthwise into one end of the appropriate specimen. The thermocouple lead wires were brought out of the probe through the center of the internal support tube, so that temperatures could be recorded continously on a stripchart potentiometer recorder. Since the computer results indicated that the temperature variation was linear for regions with a constant gap between the internal support tube and the specimens, the four temperatures accurately defined the specimen temperatures. The specimen temperatures were controlled by regulating the amount of cooling air admitted to the probe. The output from a control thermocouple, which was attached to the specimen at the same axial location as thermocouple 2, was monitored by a proportional temperature controller.

The probes were exposed in two zones of the superheater. The higher temperature location was in front of the first row of superheater tubes where the gas temperature was about 816°C (1500°F). The cooler location, with an average gas temperature of 621°C (1150°F), was at the rear of the superheater section.

The specimen materials used in this program comprised:

(1) Carbon steel (A106) comparable to that used originally for the Harrisburg superheater tubes

(2) P22 low-chromium alloy which was used as replacement tubing in the superheater

(3) Stainless steels, Types 310 and 347

(4) Incoloy 825

(5) A diffusion-bonded aluminum coating (alonized) on carbon steel.

The compositions of the alloys are shown in Table 4. The Alonized* coating consisted of aluminum diffused into steel to form an iron-aluminum alloy. The standard depth of diffusion for carbon steel is 254-381 micrometers (10-15 mils).

On completion of a probe exposure, the surface of the specimens was covered with a thin layer of corrosion product scale plus a fly ash deposit. The deposit reached a maximum thickness of about 5 cm (2 in.) in 80 hours and did not increase much with longer exposure. The deposits were removed from the probes in three sections, each covering about one third of the specimen zone. Thus variations in deposit composition as a function of metal temperature could be determined when the deposits were analyzed.

Corrosion rates were determined by weight loss measurements after removal of the reacted metal, using inhibited 10 percent H_2SO_4 while the sample was made 6 volts cathodic to a carbon anode. The corrosion rate in mils per hour was calculated from the weight loss, assuming uniform

*Alon Processing Inc., Tarentum, Pennsylvania.

TABLE 4. CERTIFIED COMPOSITIONS OF CORROSION PROBE ALLOYS

Alloy	Elements, weight percent									
	Cr	Ni	Mn	Mo	Si	P	S	C	Fe	Others
A106	–	–	0.72	–	0.29	0.026	0.014	0.26	Bal	–
P/T22[a]	2.28	–	0.37	0.98	0.31	0.018	0.011	0.12	Bal	–
310SS	24.6	21.7	1.69	0.24	0.36	0.030	0.010	0.043	Bal	0.20 Cu
347SS	18.0	12.5	1.74	–	0.55	0.025	0.018	0.05	Bal	0.8 Nb; 0.02 Ta
Incoloy 825	21.5	41.5	0.37	2.95	0.16	–	0.004	0.01	Bal	1.8 Cu; 0.07 Al; 0.98 Ti

(a) P22 and T22 have the same elemental composition. T22 designates tubing, characterized by exact OD size, while P22 indicates pipe, sized by ID. Both are under ASME pressure vessel codes duplicated by a corresponding ASTM number: for P22, ASME SA 335 and ASTM A 335; for T22, ASME SA 213 and ASTM A 213. In this program P22 specimens were used, while the Harrisburg superheater tubes are T22.

attack around the specimen surface. Corrosion rates were plotted as functions of time and temperature, and each point designated in a particular plot represents a single corrosion specimen.

EFFECT OF EXPOSURE TIME

Although short-term corrosion probe exposures characterize the corrosivity of the environment, it is necessary to have long-term exposures as well in order to obtain a curve for corrosion rate as a function of time. For this reason corrosion probe exposures of both 80 and approximately 800 hours were conducted to supplement the 8-hour exposures. The corrosion rates for carbon steel specimens are shown as a function of time in Figure 3 for the cofiring of refuse in sewage sludge. These results are compared with the corrosion data obtained previously at the Miami County Incinerator at Troy, Ohio, where bulk refuse alone was burned.[3] The data are interpolated from several specimen temperatures to a common temperature of 260°C (500°F). This temperature was selected to be similar to that of the Harrisburg Incinerator superheater tubes which operate at a steam temperature of 232°C (450°F). The data point for the 8-hour exposure time at Harrisburg when no sludge was burned with the refuse compared favorably with that from the Troy Incinerator for which longer exposure times up to 828 hours also were obtained. The corrosion rate was slightly higher at Troy because the probe was exposed to some flame radiation. The data of Figure 3 emphasize the fact that 8-hour exposure results cannot be applied to long-term exposures except for cases such as the early operation at Harrisburg, when it was the practice to use the soot blowers on the superheaters quite frequently. At that time the soot blowing was conducted as often as once on each 8-hour shift during the 5-day week of operation. This frequent soot blowing resulted in tube wastage as represented by the upper square of Figure 3 which led to a superheater tube failure after approximately 3000 hours of operation.[4] Sections of the failed tube which were not subjected to the soot blower blast showed relatively minor tube wastage. In the same time interval, the soot blown section lost 3.62 mm (145 mils), while the wastage on the untouched section amounted to only 0.38 mm (15 mils). Hence, the high wastage rate of the cleaned areas was equivalent to that measured on new specimens exposed for about 200 hours on the corrosion probe. Similarly, the uncleaned portions of the tubes gave a low wastage rate consistent with an extrapolation of the data for probe specimens exposed longer than the 820-hour test. Thus, when fresh metal is exposed at intervals by removal of deposits, the high initial corrosion rate recurs in a cyclic fashion and the long-term wastage reflects this effect. In this case the experimental data substantiate the benefits of extending the intervals between soot blowing from every shift to every month. This practice alone might extend tube life by almost a factor of eight.

The addition of sewage sludge to the refuse reduced the initial corrosion rate of the carbon steel by about a factor of two. However, as the exposure time increased, the corrosion rates for burning with and without sludge converged. Thus at the 800-hour point, the rate experienced for the small amounts of sludge burned at Harrisburg was only slightly less than that for refuse alone at the Troy Incinerator. Nevertheless, if the difference in the two curves at the 1000-hour point were to be maintained indefinitely, the result would be a 35-40 percent increase in boiler tube life for the system with sludge added.

The corrosion rates for the other alloys used in the probe exposures at Harrisburg during cofiring of refuse and sludge are given as a function of time in Table 5 for three temperatures covering the exposure range. The P22 alloy had metal wastage rates essentially the same as those for the carbon steel. Significantly lower rates were observed for the Type 310 and 347 stainless steels and the Incoloy 825.

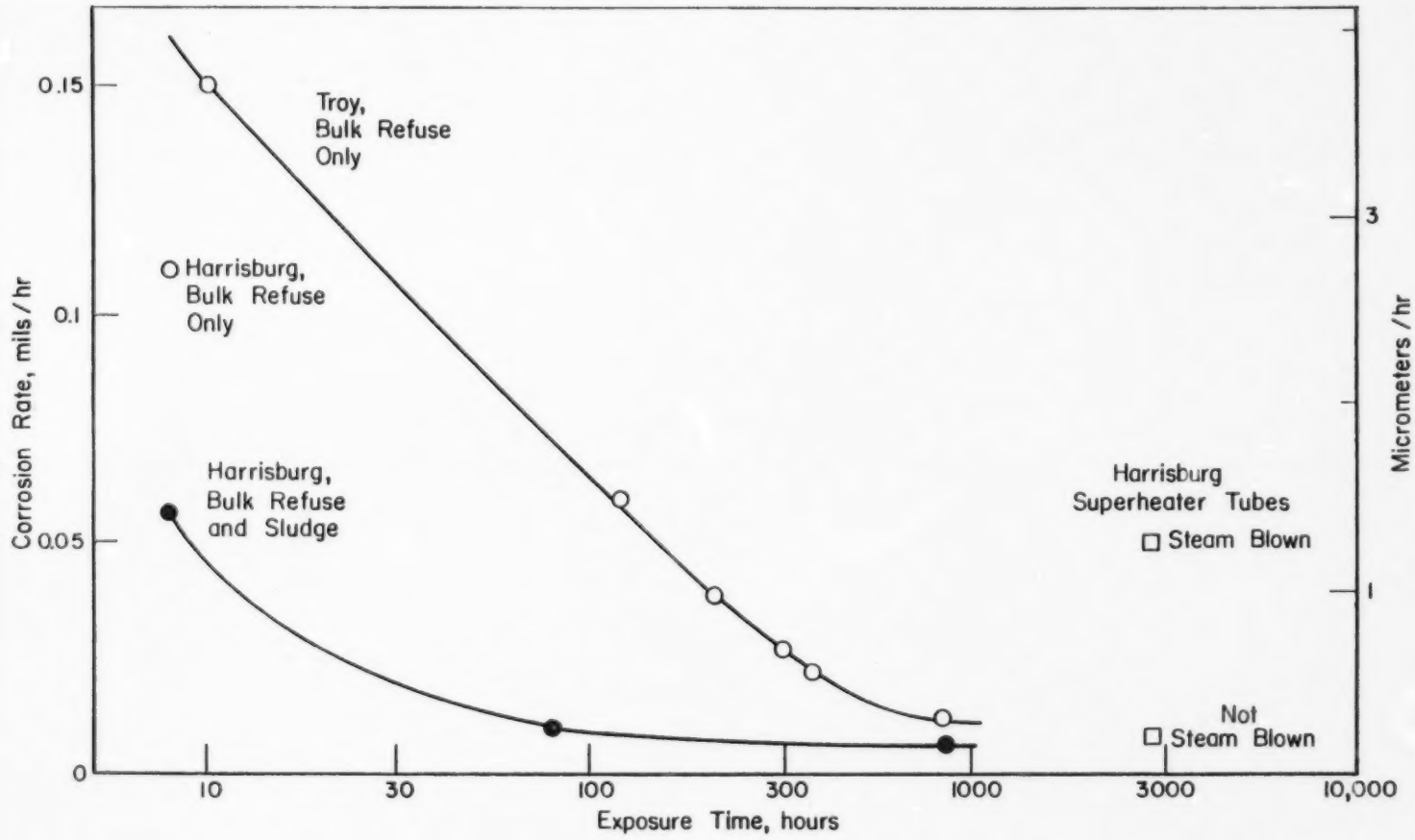

Figure 3. Corrosion rates of carbon steel at a metal temperature of 260°C (500°F) versus exposure time.

TABLE 5. CORROSION RATES FOR 8, 80 AND 816 HOUR EXPOSURES TO BURNING REFUSE WITH SLUDGE

(Interpolated to fixed temperature values)

Alloy	Metal temperature F	Metal temperature C	Wastage rate, mils/hr, for time indicated 8 hours	80 hours	816 hours
A106	500	260	0.051	0.0093	0.0082
	700	371	0.10	0.0093	0.0086
	900	482	0.132	0.0105	0.0087
T/P 22	500	260	0.059	0.0098	0.0083
	700	371	0.080	0.0096	0.0085
	900	482	0.140	0.0102	0.0090
310SS	500	260	0.024	<0.0001	0.0011
	700	371	0.022	0.0002	0.0011
	900	482	0.007	0.0009	0.0017[a]
347SS	500	260	0.038	0.0003	0.0025
	700	371	0.023	0.0011	0.0020
	900	482	0.009	0.0022	0.0020
Incoloy 825	500	260	<0.005	<0.0001	0.0011
	700	371	0.015	0.0005	0.0012
	900	482	0.014	0.0009	0.0020

(a) Similar wastage rate of .00153 mils per hour was observed for this same alloy during a 1318 hour exposure with metal temperatures averaging 890 F (±60) in the Norfolk, Virginia, Incinerator (Ref. 3).

As expected, the wastage rates of the ferritic alloys (A106 and P22) were reduced substantially for the 80-hour exposure, with less reduction for the 816-hour period. At the longer times of 80 and 816 hours the effects of temperature were reduced to the extent that the loss rates were nearly the identical value of 0.23 micrometers/hr (0.009 mils/hr) for all metal temperatures between 177 and 454°C (350 and 850°F). The extrapolation of the corrosion rates to longer times would suggest wastage rates that gradually decrease to values well below those measured. The observed rates of 0.20-0.25 micrometers/hr (0.008-0.01 mils/hr) would indicate boiler tube life of only 2 to 3 years, but there has been no further evidence of rapid deterioration of tubes at Harrisburg since the corrective measures were taken. Consequently the corrosion rates shown in Figure 3 will most likely decrease further with time by a factor of 5 to 10.

Less predictable trends were observed in the wastage of the austenitic steel specimens. As a rule the stainless steels 310, 347 and Incoloy 825 showed wastages equivalent to a fifth or less of that for the ferritic steels. The most durable appeared to be either the 310SS or the Incoloy 825 both of which were only slightly better than 347SS in corrosion resistance. All three of these alloys showed an anomalous increase in wastage rate for the longest exposure time of 816 hours. This fact suggests that furnace operating conditions were different in the longer exposure period. Examination of the incinerator operations log showed that less sludge than usual was burned in the month after the incinerator resumed operation following the pit fire. The corrosion data obtained at the Troy Incinerator several years ago showed that the high alloy steels responded more dramatically than ferritic steels to sulfur additions to the refuse. A similar effect may have occurred at Harrisburg when less sludge was burned than during the shorter term runs.

In comparing previous wastage rate data for austenitic steel, the closest condition was for 310 stainless steel in the Norfolk, Virginia Incinerator. These data were centered about a wastage rate of about 0.041 micrometers/hr (0.0016 mils/hour) and a metal temperature of 460°C (860°F) for exposure times of 180, 188, and 1316 hours. Thus, rates of this magnitude for austenitic alloys are not unusual in the incinerator environment.

EFFECT OF METAL TEMPERATURE

The surface temperatures of boiler tubes may be as much as 50°F greater than that of the steam temperature inside. When water treatment is adequate, interior scaling will be minimal and will not contribute to increased metal temperature, but buildup of deposits on the interior of the tube may result in significantly higher temperatures at that point. Consequently, the probe operation was designed to provide specimen temperatures which would cover a wide operating range. A plot of wastage rates for A106 carbon steel over the temperature range 300-800°F for 8 hours exposure to the burning refuse with and without sludge additions is shown in Figure 4. The line drawn on this figure from studies conducted at the Troy, Ohio, Incinerator is based upon 10 or more A106 carbon steel specimens, exposed at a gas temperature of 816°C (1500°F), which is comparable to that of the Harrisburg probe in the superheater inlet. The increase in corrosion rate starting at 427°C (800°F) is typical of that found throughout this program for carbon steel and low alloy steels in burning of bulk refuse at high gas temperatures. The three data points obtained for the carbon steel exposed to comparable conditions in the Harrisburg Incinerator fall close to the curve established for the Troy Incinerator. The corrosivity of the environment was significantly reduced when the sewage sludge was burned with the refuse. As shown in Figure 4, the 8-hour corrosion rates with sludge present in the fuel are 2 to 2.5 times lower than those with refuse alone.

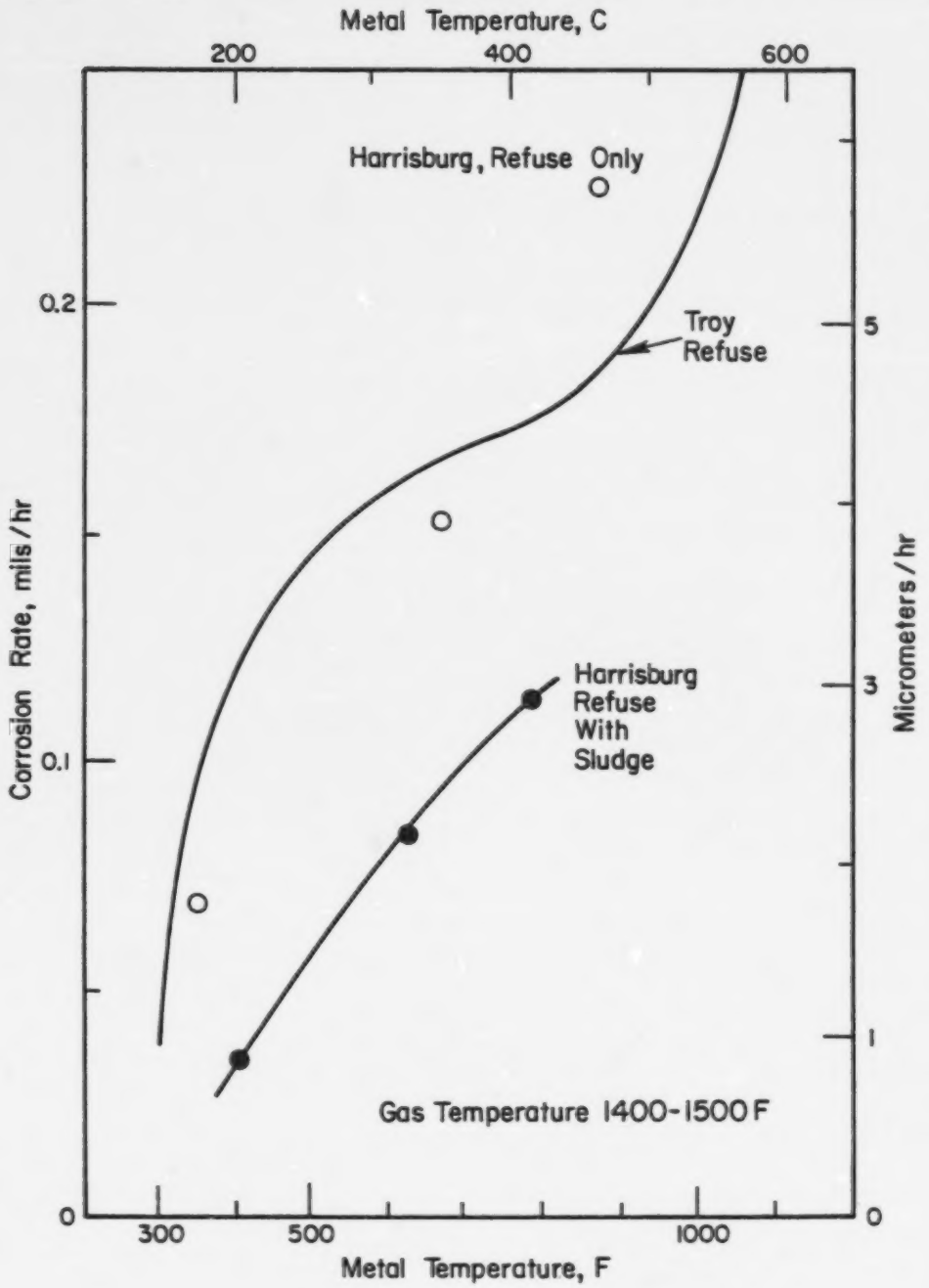

Figure 4. Corrosion rates of carbon steel (A-106) specimens exposed for 8 hours to burning refuse alone and with sludge.

Similar conditions and results are shown in Figure 5 for the low chromium alloy (T22) now being used for the superheater tubes in the Harrisburg Incinerator. The difference in corrosivity of the two fuels becomes more pronounced for both alloys as the metal temperature increases. Here again the line drawn in the figure was obtained at Troy for a similar low-chromium alloy (T11). In comparing the performance of carbon steel and P22 when the sewage sludge was burned with the refuse, little difference was observed in the corrosion rates, as noted in Figures 4 and 5. When refuse alone was burned, the corrosion rate for P22 alloy was slightly lower than that of A106 at temperatures up to 370°C (700°F). However, at about 427°C (800°F) there was little difference in the corrosion rate of the two materials. These results indicate that the reduction in tube failures at the Harrisburg Incinerator in recent years was not greatly influenced by replacing carbon steel tubes with the T22 alloy.

On the basis of their performance in previous incinerator studies, two austenitic stainless steels, Types 310 and 347, were selected for this program. In addition, Incoloy 825 was chosen because it has demonstrated very low corrosion rates in the incinerator environment. These stainless steels are employed in large utility boilers for superheater tubes where steam temperatures of 538°C (1000°F) or higher occur. Incoloy 825 is approved as a material of construction under the Boiler and Pressure Vessel Code of the American Society of Mechanical Engineers for temperatures up to 538°C (1000°F), although the high price of this alloy has limited its use. These alloys obtain their corrosion resistance through the formation of spinel structures on the surface as a result of their high chromium and nickel content. These spinels are mixed oxides, are less volatile, and adhere better to the metal surface than either the iron or chromium oxides which form as a protective layer on carbon or low-alloy steels.

Another corrosion-resistant material employed on this program was an "Alonized" coating. This coating consisted of an aluminum-rich layer about 381 micrometers (15 mils) thick applied to the A106 carbon steel by a pack-aluminizing process. This process forms layers of hard intermetallic aluminum-iron compounds with the capability of forming a corrosion resistant aluminum oxide on the outer surface.

These alloys showed very low wastage rates in the aggressive incinerator environment as summarized in Figure 6. In comparable 8-hour exposures the corrosion of these alloys at temperatures between 260°C (500°F) and 482°C (900°F) were only about one-fifth as great as those for the carbon steel and the low-alloy steel. These high chromium-nickel alloys afforded more protection as the temperature increased, probably due to more rapid diffusion of the chromium and nickel into the oxide layer with the formation of a thicker protective scale. The addition of sludge to the refuse has practically no effect on the corrosion rates of Types 310 and 347 stainless steel. The sludge did, however, slightly reduce the attack on Incoloy 825, particularly at lower temperatures.

EFFECT OF GAS TEMPERATURE

The experience with boiler operation at Harrisburg demonstrated the typical increased attack of boiler tubes at higher temperatures in that first the upstream superheater tubes failed and then the more remote banks failed. Although convective and radiant heat transfer ratios fluctuate rapidly with dynamic changes in the combustion process and flame temperature, tube metal wastage rates are in general lower in sites at which the gas temperature is lower. For this program two different locations for probe exposure were selected on the basis of their relative gas temperatures. The higher temperature location was in front of the first superheater bank and 6 feet below the

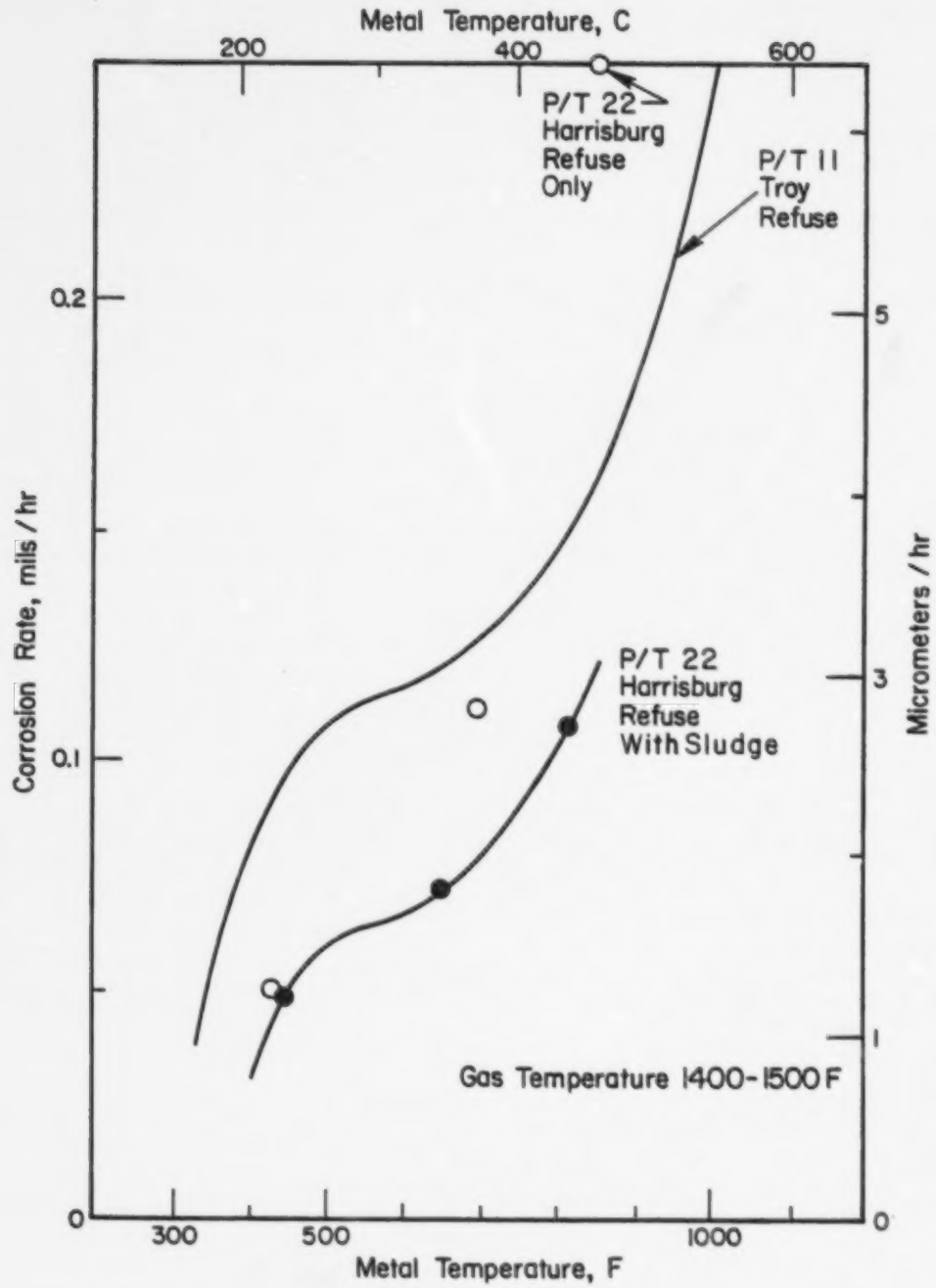

Figure 5. Corrosion rates of low chromium alloys exposed for 8 hours to burning refuse alone and with sludge.

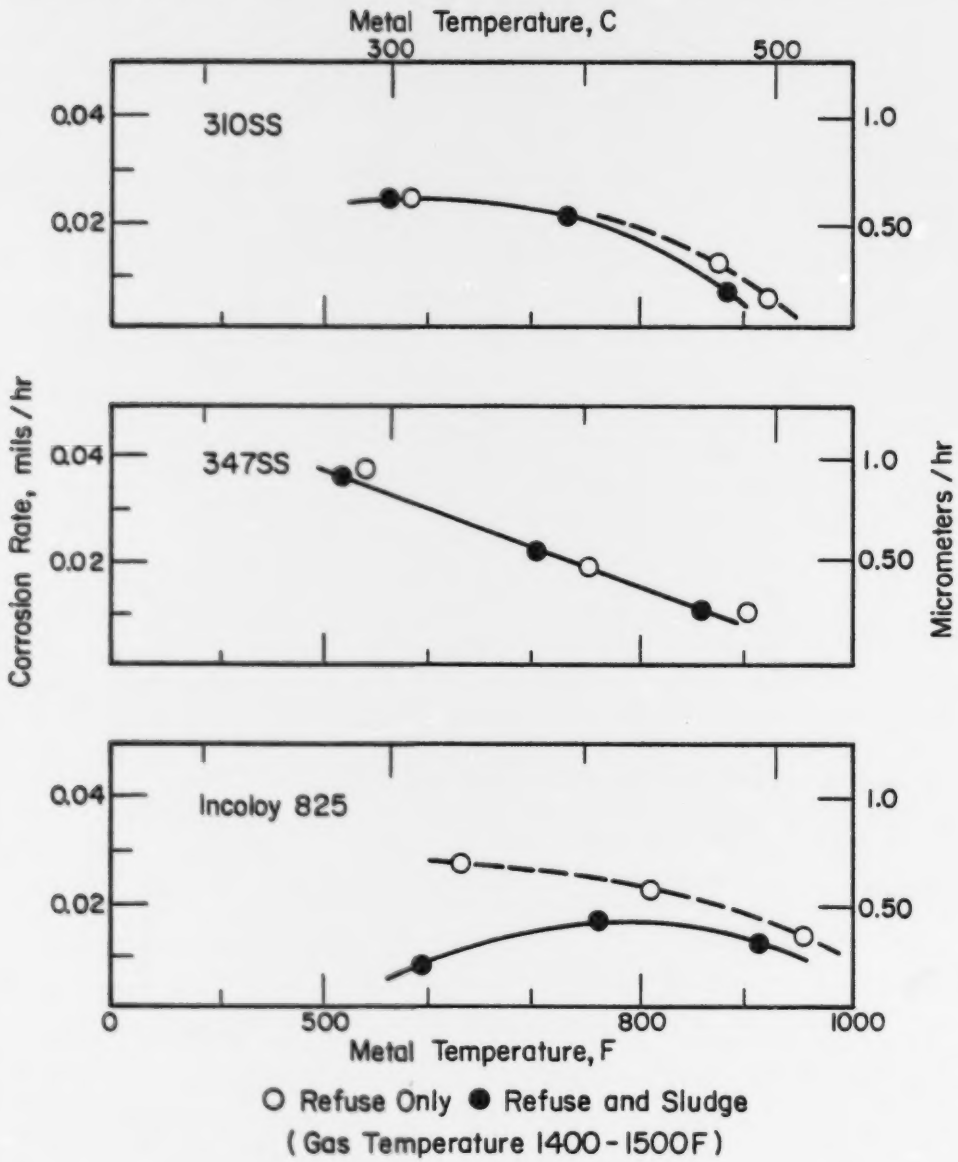

Figure 6. Corrosion rates of stainless steels and Incoloy 825 versus metal temperature (8-hour exposure).

location of the plant thermocouple for furnace temperature measurement. Gas temperatures in this zone are monitored and maintained near 815°C (1500°F). At this point the gas flow reversed from the upward flow in the combustion chamber to a somewhat downward flow through the superheater. Flakes of burning refuse carried in the flue gas stream resulted in relatively high temperature and a blizzard of impinging particles. Photographs of the corrosion probes were taken in an effort to establish temperature fluctuations at this high-temperature viewing port. Despite the large momentary changes in brightness in this region the temperature of the exposed probe thermocouple and the protected plant thermocouple were relatively stable. The plant thermocouple consistently read about 83°C (150°F) higher than the probe thermocouple.

Two of the 8-hour probe runs were made in a relatively cool location which was about 15 feet downstream of the hotter location. At this point the tubes were practically black and the gas temperature as monitored by the probe thermocouple was in the range 593-650°C (1100-1200°F). This drop in gas temperature and lack of heat transfer from radiant surroundings permitted adequate probe cooling with only a modest amount of cooling air of about 0.14 to 0.28 m^3/min (5 to 10 cfm) as compared to the 0.56 to 0.85 m^3/min (20 to 30 cfm) required in the high-temperature location. The corrosion rates of the carbon steel and the P22 alloy (Figure 7) exposed at low gas temperature showed only a slight variation with metal temperature as compared to Figures 4 and 5 where the corrosion rates increased rapidly with metal temperature when exposed to high gas temperature. The corrosion data demonstrated that the same temperature dependence existed at low gas temperature when the sludge was burned with the refuse. Under these low temperature conditions, there was no apparent difference in the corrosion rates between the carbon steel and the P22 alloy.

It should be noted that a reduction in gas temperature is more effective in reducing the corrosivity of the environment over the entire metal temperature range than is the addition of sludge to the fuel. Thus, although additives to the refuse may improve the life of boiler tubes, a boiler design which would reduce the temperature in the steam generator section would also provide a significant improvement in boiler tube life.

EFFECTS OF "ALONIZING"

Due to the nature of the coating process, the durability of the "Alonized" specimens could not be measured quantitatively. Both the thickness and the reaction depth of the coating varied from sample to sample and were measured only after sectioning for metallography following the exposure. As applied to the A106 steel, the coating thicknesses ranged from 9 to 18 mils. The variation of thickness in different locations on single samples amounted to only 1 to 6 mils after exposure. In all cases a protective iron-rich intermetallic compound remained intact on the parent metal. This innermost layer (probably Fe_3Al) was at least 3 mils thick. The outermost layer, possibly $FeAl_3$, showed occasional fissures as deep as 9 mils but usually about 3 to 4 mils. Thus the "Alonizing" demonstrated complete protection during exposures of 8, 80, and 816 hours, for average metal temperatures between 204 and 443°C (400 and 830°F).

FLUE GAS ANALYSES

The composition of the furnace gases in the location of the higher temperature probe was determined for refuse burning with and without sewage sludge. Standard EPA sampling techniques

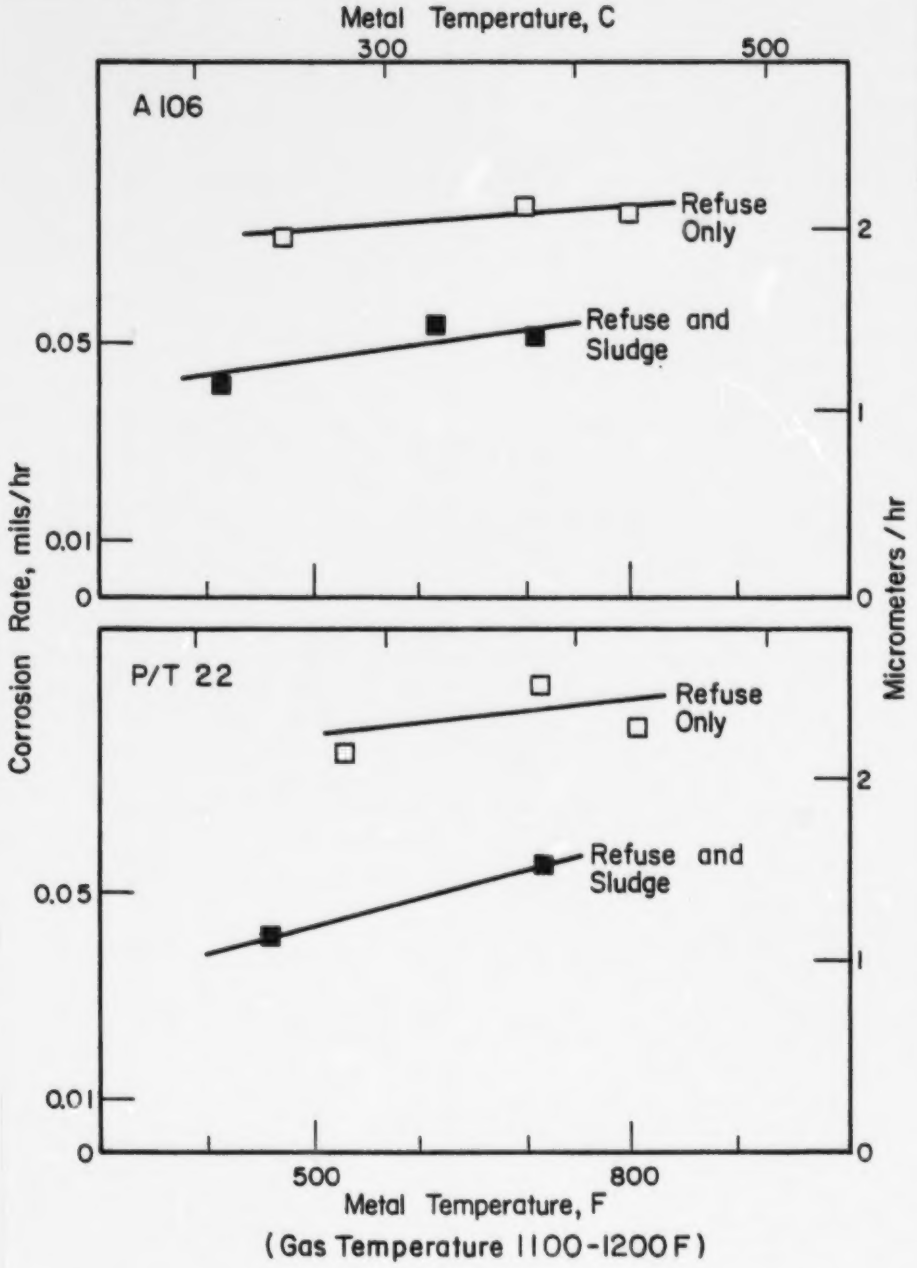

Figure 7. Corrosion rates of carbon and low alloy steel versus metal temperature (8-hour exposure).

were used for measurement of sulfur oxides, nitrogen oxides, and furnace particulate collection. HCl concentrations were determined by measuring the chloride content of the impingers in the sulfur oxides train. Oxygen and CO_2 were measured by Orsat analysis of a bag sample of the gases accumulated during a run. The CO and organic compounds were determined by mass spectrometer analysis of grab samples taken in evacuated bulbs. The results of the measurements are summarized in Table 6.

The data show that more SO_2 was present in the flue gases when sewage sludge was burned than when refuse was burned alone. This result is indicative of the additional sulfur contributed by the sludge, which would inhibit chloride corrosion. There also was less HCl in the combustion gases when sludge was burned, indicating some dilution of the refuse by the low chloride sludge. The other gas components that were measured did not show much difference in concentration for the two fuel compositions. An increase in moisture was observed when the sludge was burned, reflecting the high moisture content (75 percent) of that material. The completeness of combustion is indicated by the low concentrations of carbon monoxide and methane. The gas samples were examined for other hydrocarbons in addition to methane, but their concentrations all proved to be below the detection limit of 0.1 ppm.

PARTICULATE ANALYSES

The particulate matter in the flue gas stream was collected on a filter during the flue gas sampling, both with and without sewage sludge added to the refuse. In addition, fly ash from the electrostatic precipitator hopper was sampled on these same two occasions. These solids were analyzed for sulfur and chlorine by wet chemical methods and for metals by optical emission spectroscopy. The results of the analyses are shown in Table 7.

The particulates in the superheater zone showed significant difference in composition with respect to sulfur and calcium content, both being higher when sludge was included in the fuel. By contrast, the aluminum concentration was greater when refuse alone was burned. The chlorine content was only slightly higher for the refuse without sludge. One unusual feature was the presence in one sample of a large amount of antimony, which is ordinarily a minor constituent of refuse. Antimony compounds are used as flameproofing agents in some textiles and plastics, and it may have been present in a batch of such materials in the waste.

With respect to corrosive influences, the higher sulfur content of the particulate for the refuse-sludge combination has the most significance. If the fly ash is converted to sulfates before it deposits on the boiler tubes, corrosion is minimized. This sulfate formation correlates with higher SO_2 concentration found in the flue gases when sludge was burned with the refuse.

There were some significant differences in composition between the precipitator ash and the fly ash in the superheater zone. The precipitator ash contained: (1) more magnesium and silicon, and (2) less sulfur, chlorine, lead, zinc, and tin. These differences indicate that the heavier metals were deposited, probably as sulfates and chlorides, on the boiler surfaces as the flue gas stream passed through the boiler. The magnesium and silicon could well have formed magnesium silicates, which have relatively low density and would be carried through to the precipitator. The addition of the sludge did not have any important effect on precipitator ash composition.

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TABLE 6. COMPOSITION OF FLUE GASES AT HARRISBURG INCINERATOR

	Flue gas composition for fuel indicated	
	Refuse	Refuse & sewage sludge
SO_2, ppm	135	240
SO_3, ppm	4	3
HCl, ppm	485	345
NO_x, ppm	106	84
O_2, %	9.0	8.5
CO_2, %	7.5	9.5
CO, %	0.03	0
H_2O, %	8.8	9.8
CH_4, ppm	10	17

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TABLE 7. ELEMENTAL ANALYSES OF GASBORNE PARTICULATES

Element	Composition, weight percent			
	Superheater zone		Precipitator ash	
	Refuse	Refuse + sludge	Refuse	Refuse + sludge
Si	5–10	4–8	20–40	15–30
Al	15–25	4–8	10–20	7–9
Ca	4–8	10–20	10–20	8–12
Fe	1–3	1–3	2–4	2–4
S[a]	4.5	10.6	3.2	3.3
Pb	2–4	2–4	1–3	0.8–2
K	5–10	8–15	4–8	2–4
Mg	0.8	0.6	2–4	1–3
Zn	8–15	5–10	2–4	2–4
Na	5–10	5–10	2–4	1–3
Cl[a]	8.3	7.3	3.4	3.6
Sn	1–3	2–4	0.3	0.2
Ti	0.8	0.6	1–3	1–3
Cu	0.2	0.1	0.05	0.1
Cd	0.2	0.2	<0.1	0.05
Ba	0.06	0.06	0.2	0.08
Cr	0.2	0.05	0.08	0.05
Sb	5–10	0.2	0.05	0.1
Mn	0.08	0.06	0.2	0.2
Zr	0.01	<0.01	0.02	0.03
Ni	0.02	0.01	0.03	0.02
V	0.01	<0.01	0.02	0.02
Mo	0.02	0.01	0.01	<0.01
Ag	0.04	0.01	0.01	<0.01
B	0.06	0.05	0.04	0.04
Bi	0.03	0.01	0.01	<0.01
Co	<0.01	<0.01	0.01	<0.01
Ga	0.02	0.02	<0.01	Nil
Sr	0.01	0.02	0.02	Nil

(a) Wet chemical analysis for total sulfur and chlorine; others by optical emission spectroscopy.

DEPOSIT AND CORROSION PRODUCT ANALYSES

Since the corrosion probe and boiler tubes were not soot-blown during any of the experiments, all specimens collected particulate deposits and sometimes an appreciable layer of iron oxides and corrosion product "scale" which was originally the outer surface of the metallic specimens. Photomicrographs of a typical deposit and scale are shown in Figure 8. Susceptible metals produced porous scales up to about 1.3 mm (0.05 inch) thick. Over the scale of metallic oxides were thicker layers of deposited particles. These ranged from about 1.6 to 12.7 mm (0.06 to 0.5 inch) in thickness after the 8-hour exposures and about twice that for the 80- and 816-hour runs. These loose deposits were brushed from the probe and identified by their location on the probe in three groups: i.e., specimens 1 through 6 for low metal temperatures, specimens 7 through 12 for moderate, and specimens 13 through 18 for highest metal temperatures.

Deposits were individually analyzed by wet chemistry for total sulfur and chlorides. As in prior studies, chlorine levels were higher for lower metal temperatures and briefer exposure times. All values are tabulated along with the optical emission analyses for metals in Table 8. High chloride levels are associated with the rapid early attack of exposed metal. However ferric chloride decomposes at temperatures above 315°C (600°F), leaving little trace of chloride but leaving a porous iron structure susceptible to oxidation. The eventual oxidation products may be influenced by the nature and composition of the ensuing deposits. Previous work on this program demonstrated the function of a sulfur-bearing fuel in converting chlorides to sulfates prior to deposition. The sulfates accumulate in the slag and deposits and thus prevent corrosion by HCl and chlorine.

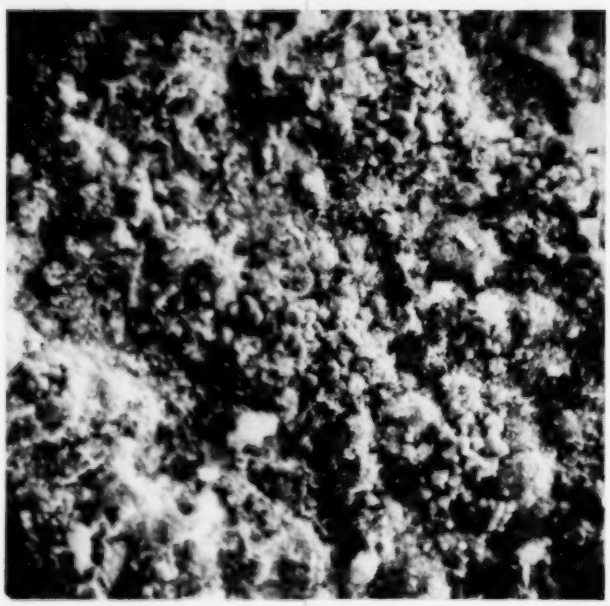
As a long-term result, the tube life is extended while the sulfur accumulates and the chloride remains in the gaseous phase. Thus the amount of sulfur remains near 8 to 10 weight percent for deposits collected over 8, 80, or 816 hours for all regions of the corrosion probe. However the concentration of chlorides falls from 3 to 5 percent for deposits on cool tubes exposed 8 hours, down to practically zero chloride in deposits collected during the 816-hour exposure (Probe 46). During this same range of exposure times, the amounts of heavy metals associated with the sulfates remain relatively constant. These elements are calcium, potassium, sodium, lead, magnesium and zinc.

Chlorides were easily identified only in the short-term deposits next to the tubes with metal temperatures below 600°F. However, weak X-ray diffraction patterns for sodium chloride were identified on two of the three scale samples examined. Even stronger evidence for the earlier presence of iron chloride was the strong, X-ray diffraction pattern for β-FeOOH. This compound is the product of hydrating the iron chloride. Other compounds identified by X-ray diffraction in the metallic scale include iron sulfide and iron oxides (magnetite, hematite, and wustite).

In the loose deposits, the major compounds identified were silica or quartz, calcium sulfate, and iron oxides. Many of these particles were spheroids and had probably melted in the combustion zone (Figure 8). Selected deposits were analyzed by energy dispersion of their X-rays (EDAX) to confirm and to localize the elemental analyses from optical emission spectroscopy.

Also, with EDAX technique a reasonable level of chloride was detected in the oxide scales removed from two carbon steel specimens on the 80-hour probe and in the edge of a surface pit in a P22 specimen from that probe. Typical X-ray intensities of the chlorides averaged about a tenth that of iron as the parent metal basis. These chlorine values of 0.04 and 0.17 are shown with Figure 9. In the intact shells of oxide peeled from the carbon steel specimens, the chloride intensity was

500X Deposit



500X Scale

Figure 8. Outer deposit and inner scale removed from exterior of carbon steel (A-106) specimen.

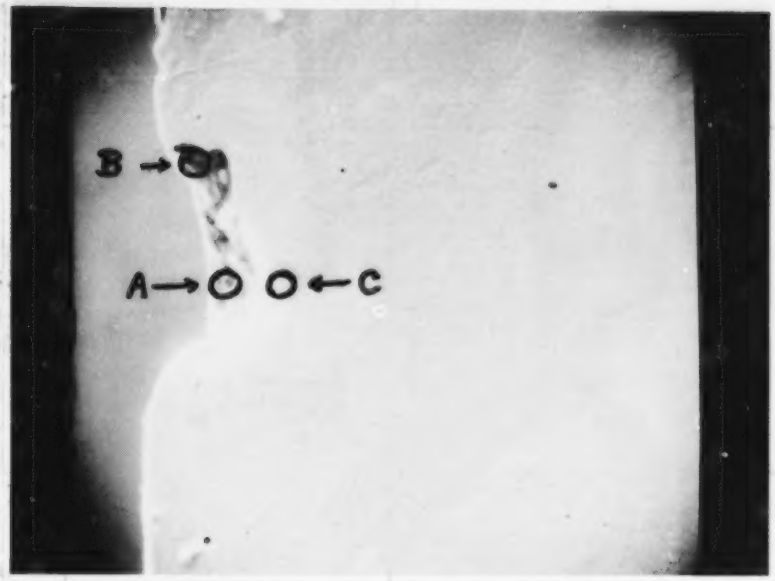
TABLE 8. ELEMENTAL ANALYSES OF DEPOSITS ON CORROSION PROBES

Probe No.	Composition, weight percent																	
	41			42			43			44			45			46		
Temperature Zone[a]	L	M	H	L	M	H	L	M	H	L	M	H	L	M	H	L	M	H
Element																		
Si	7	7	7	6	6	6	6	6	6	6	6	6	10	8	10	8	8	8
Al	7	7	7	7	7	7	4	4	4	4	5	4	4	3	4	5	6	8
Ca	11	11	14	6	6	6	10	10	10	10	10	10	8	10	10	10	10	10
Fe	3	2	2	3	3	3	2	2	2	2	2	2	3	4	3	8	3	8
S[b]	8.0	9.5	8.2	8.1	8.8	9.3	10.4	11.5	10.5	8.5	9.6	9.5	7.7	10.6	10.7	11.3	9.7	10.2
Pb	4	4	2	6	11	11	5	3	3	4	10	10	5	0.5	4	4	4	4
K	7	14	14	6	7	11	6	6	6	2	3	3	3	5	6	6	4	6
Mg	0.8	0.8	0.8	0.8	0.8	0.8	1	1	1	1	1	1	1	1	2	1	1	1
Zn	4	4	4	5	5	5	5	5	5	5	8	8	4	3	6	3	3	3
Na	6	6	6	6	6	6	6	4	5	2	3	3	5	5	6	3	3	3
Cl[b]	5.6	1.5	0.4	3.3	2.2	1.8	0.5	0.1	0.04	2.9	1.8	1.8	4.6	0.3	1.4	0.01	0.01	00
Ti	0.8	0.8	0.8	0.8	0.8	0.8	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Cu	0.05	0.05	0.05	0.05	0.05	0.05	0.1	0.1	0.1	0.1	0.1	0.1	0.3	0.1	0.2	0.1	0.1	0.1
Cd	0.1	0.1	0.05	0.05	0.05	0.05	0.1	0.08	0.08	0.08	0.2	0.1	0.1	ND	0.1	0.1	0.08	0.1
Ba	0.1	0.1	0.1	0.06	0.06	0.06	0.05	0.05	0.06	0.06	0.06	0.04	0.08	0.08	0.08	0.06	0.06	0.06
Cr	0.2	0.2	0.2	0.5	0.5	0.5	0.05	0.05	0.05	0.08	0.08	0.05	0.1	0.8	0.1	0.5	0.08	0.4
Sb	0.08	0.08	0.05	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.5	0.3	0.5	0.1	0.08	0.08
Mn	0.2	0.2	0.1	0.1	0.08	0.08	0.01	0.01	0.01	0.02	0.02	0.02	0.2	0.2	0.2	0.05	0.01	0.04
Zr	0.01	0.01	0.02	0.01	0.01	0.01	0.02	0.01	0.03	0.02	00	00	0.02	0.02	0.02	0.02	0.05	0.04
Ni	0.6	0.06	0.06	0.2	0.1	0.1	0.03	0.03	0.05	0.05	0.02	0.02	0.03	0.2	0.1	0.2	0.1	0.5
Sn	0.6	0.6	0.4	0.8	0.8	0.8	0.2	0.1	0.1	0.2	0.4	0.5	0.2	0.2	0.3	0.5	0.1	0.4
V	0.02	0.02	0.02	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.01	0.01	0.01	0.02	0.02	0.02
Mo	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.01	0.01	0.02	0.02	0.01	00	0.02	00	0.05	0.01	0.04
Ag	0.01	0.01	0.01	0.01	0.01	0.01	00	00	00	00	00	00	00	00	00	00	0.01	0.01
B	0.02	0.02	0.03	0.03	0.02	0.02	0.02	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.02	00	0.01	0.01
Bi	0.01	0.01	0.01	0.01	0.01	0.01	00	00	00	00	00	00	00	00	00	0.01	00	0.01
Co	00	00	00	00	00	00	00	00	00	00	00	00	00	00	00	0.01	0.02	0.02

(a) Specimens from each probe were subdivided into groups from three metal temperature regions: L for low (300 to 600°F), M for medium (500 to 800°F), and H for high (700 to 1000°F).

(b) Wet chemistry techniques were used for sulfur and chlorine only. Others were semiquantitative, optical emission spectroscopy.

Note: 00 = barely detectable.



600X

Location	Normalized EDAX Intensities					
	Al	Si	S	Cl	Cr	Fe
A	0.02	0.69	0.03	0.04	0.02	1.00
B	0.12	0.18	0.18	0.17	0.55	1.00
C*	tr	tr	tr	0	0.04	1.00

*Base metal showed only iron and chromium as major ingredients of P 22. Other elements are residues from waste burning not completely removed by electrolytic cleaning process.

Figure 9. Cross section of pit in P-22 specimen (80-hour exposure).

0.12 and 0.02 of the iron intensity, respectively. Hence chlorides were positively identified at the bottom of pits and at the interface between sound metal and scaling oxides, demonstrating participation by chlorine in the corrosion reactions. On the other hand, chlorides were not detected in the outer layers of deposited particles.

SECTION 6

METALLOGRAPHIC EVALUATION OF CORROSION PROBE SPECIMENS

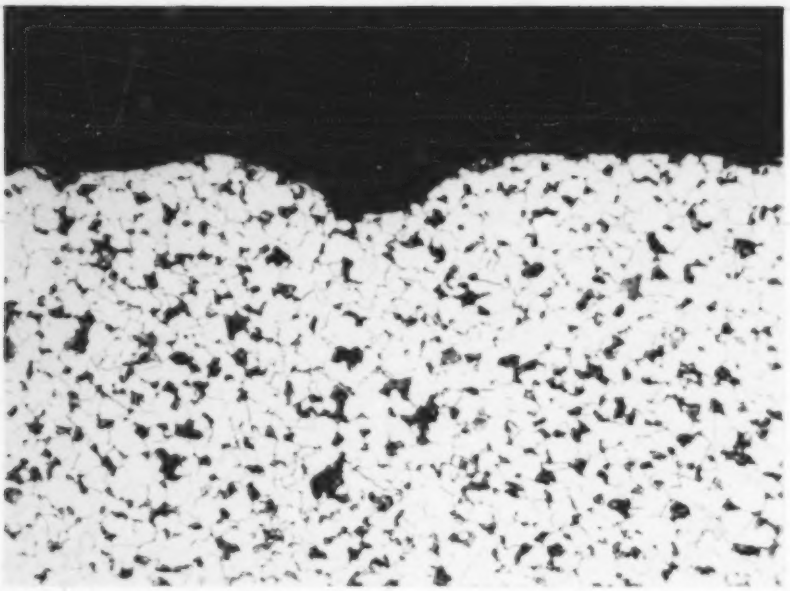
Most of the uncoated specimens were electrolytically stripped of oxide prior to metallography. Selected samples of each alloy were then sectioned and examined metallographically to determine the nature of the corrosive attack. The most important effects were observed on the specimens discussed in this section principally from the 80-hour probe exposure. As a rule, the region of deepest attack was photographed.

Evaluation of the coated specimens was limited to metallographic inspection. These Alonized specimens were best prepared by embedding the specimens (often with the adherent deposits) before sectioning and polishing. Otherwise some of the protective but brittle intermetallic compounds were lost as a result of the sectioning and polishing processes.

General surface attack was observed for the probe specimens of both the original carbon steel and the low alloy P/T22 used for superheater replacements at Harrisburg. Figure 10 shows the typical sections from metals exposed for 80 hours with average metal temperatures between 427 and 454°C (800 and 850°F). In the upper view, A of Figure 10, is a section of the carbon steel A106 while the lower view, B, shows similar attack on the surface of the P22 alloy containing 2.2 percent chromium. The wastage patterns of the two materials are similar and parallel the observed weight losses of 1.06 and 1.04 grams for these A 106 and P22 specimens in adjacent positions on Probe 43.

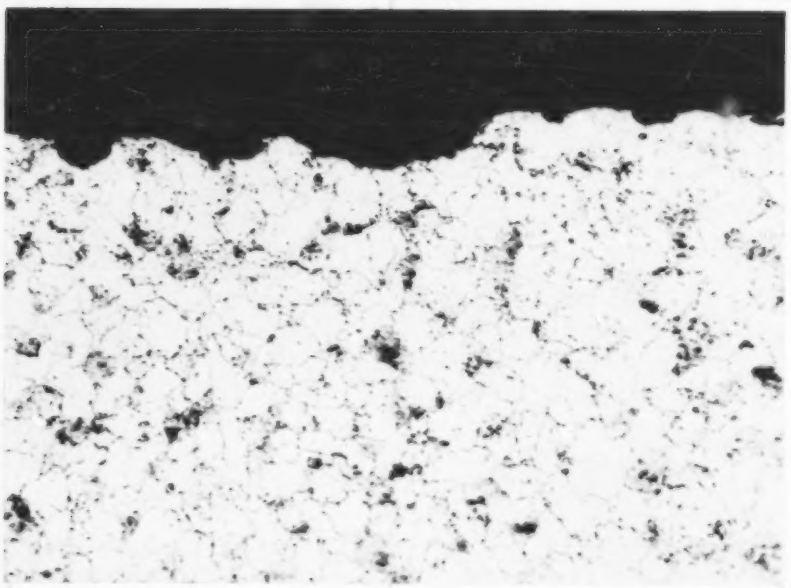
Localized surface attack in the form of pits was noted in the high chromium alloys. Figure 11 shows the infrequent intergranular attack with slight pitting in Type 310 stainless steel. It was less resistant than Type 347 stainless steel to fireside wastage under these particular conditions. The lower photograph (Figure 12) shows a large pit in a specimen of Incoloy 825. Here also the weight losses paralleled the losses shown metallographically. The 310 stainless steel specimen lost 0.060 g while the Incoloy 825 specimen lost 0.103 g at average metal temperatures of 482°C (900°F) and 491°C (916°F), respectively.

A potential corrosion mechanism which was not studied during the Harrisburg exposures was stress-corrosion cracking of the austenitic steels. Because the normal probe exposures do not include stressed specimens, no effort was made to observe this effect. However, the potential for this type of attack was present, as indicated by X-ray identification of β-FeOOH on various specimens. This compound was most likely generated by hydration of iron chloride after cooldown of the incinerator following the fire which occurred in the refuse pit during the 800-hour exposure. Although the



250X

A. Carbon Steel (A 106), 80-hour exposure



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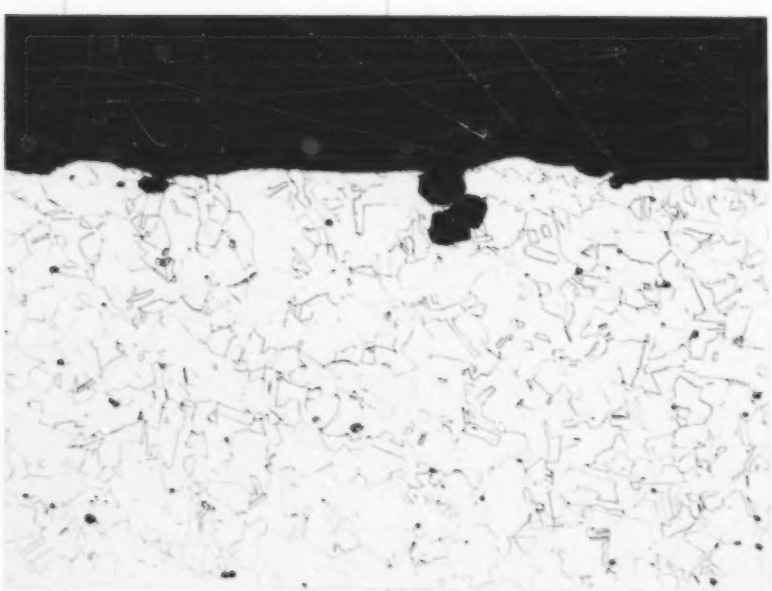
B. Low Chromium Alloy (P22), 80-hour exposure

Figure 10. Corrosive attack on steel specimens of same materials as Harrisburg superheater tubes.

250X

Figure 11. Pitting by intergranular attack in stainless steel (310), 80-hour exposure.



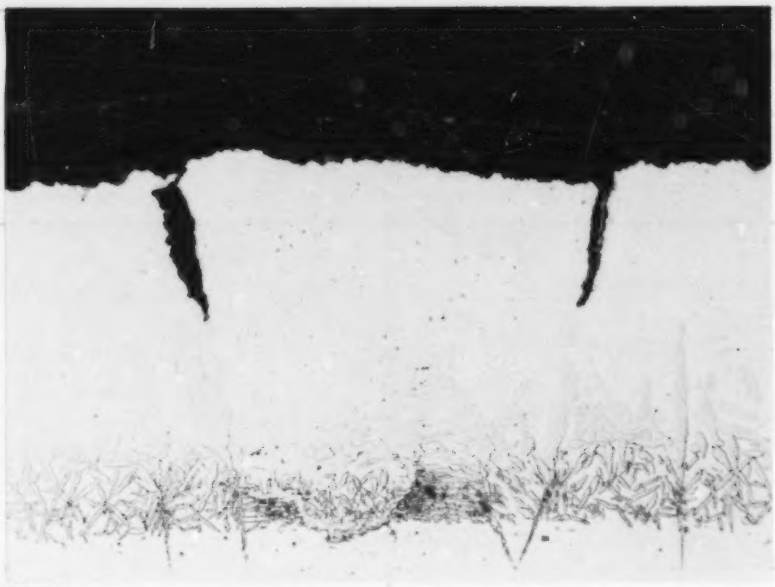
250X

Figure 12. Pitting of Incoloy 825, 80-hour exposure.

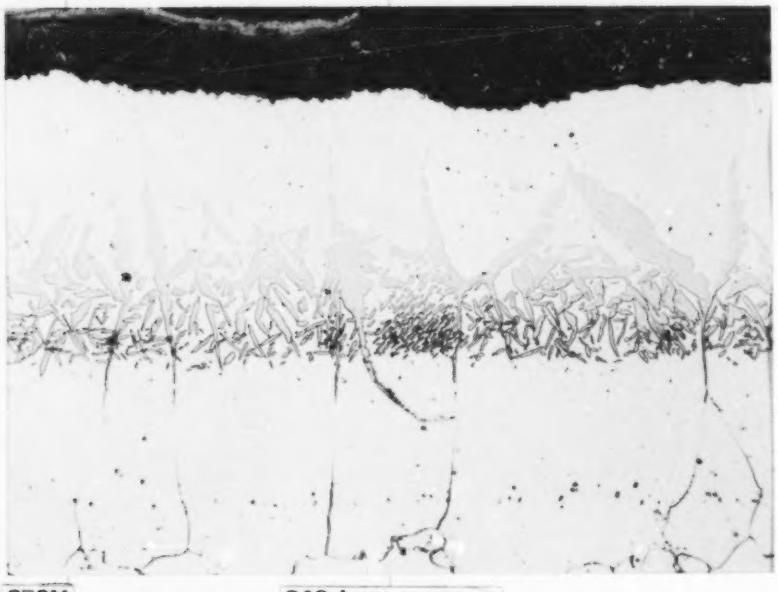
specimens were not exposed to spray from the fire hoses, the probe and samples were not protected from atmospheric moisture pickup until the unit was secured for cleanup several hours after the pit fire.

Similar exposures to moist air, marine atmospheres, or lancing of slag deposits with high pressure water can increase the chloride attack possible in damp environments, as compared to that occurring in the dry environment of sustained incinerator operation. Under such conditions the austenitic alloys may be more susceptible to failure than indicated by the wastage rates observed on the probe specimens.

Photomicrographs of the Alonized coating on the surface of carbon steel after the 816-hour exposure are shown in Figure 13. The upper view shows an atypical fissure. These were usually rare and often occurred where the alloyed layer was thickest. EDAX analysis revealed the expected intermetallic phases between the outer aluminum-rich phase through at least four intermediate phases to the iron-rich base metal of carbon steel A106. Practically all of the weight loss on these samples was attributed to oxidation on the interior (air cooled) side of the specimens. As judged by inspection of the fireside surface, it remained intact and protective. The durability of the Alonized coating may be attributed to successful wetting of the surface during application of the coating, insuring complete coverage. This was not the case with other types of coatings applied by plasma spray which were evaluated by exposure in the Troy Incinerator.



250X 816-hour exposure



250X 816-hour exposure

Figure 13. Integrity of Alonized coating on A-106 steel.

(Note that fissures have developed in the thicker coating.)

REFERENCES

1. Engdahl, R. B., et al., "Final Report on Harrisburg Municipal Incinerator Evaluation", Battelle's Columbus Laboratories, December 17, 1973.

2. Vaughan, D. A., et al., "A Study of Corrosion in Municipal Incinerators", Progress Report by Battelle's Columbus Laboratories to Solid Waste Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio, April 25, 1973. (NTIS No. PB221851).

3. Miller, P. D. and Krause, H. H., "Corrosion Studies in Municipal Incinerators", U.S. EPA Report SW-72-3-3, 1972.

4. Letter Report to Gannett, Fleming, Corddry, and Carpenter, Inc., Harrisburg, Pa. from Battelle's Columbus Laboratories, September 14, 1973.

APPENDIX A

FURNACE TEMPERATURE MEASUREMENT

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APPENDIX A

FURNACE TEMPERATURE MEASUREMENT

During some of the probe exposures an attempt was made to record photographically the rapid temperature fluctuations in the vicinity of the probe. These films suggest that combustion conditions cause more rapid temperature fluctuations than can be recorded from thermocouples in the gas stream. As a result there is a real possibility for fly ash to melt and promote liquid-phase reactions, with subsequent pitting attack on the probe specimens or on boiler tube surfaces.

The view in Figure A-1 show the appearance of the probe as seen from immediately above the axis of the probe. For these views a flag of Type 304 stainless steel foil, 1 mm (0.040 inch) thick was cemented to the thermocouple used to record the gas temperature. Its width permitted easy insertion and a large enough image to be measured densitometrically. That is, the light-stopping power of the image could be measured and compared to the average temperature of the thermocouple in the same remote location in the hot zone.[1]

During the five minutes for photographing these frames (19 to 22), the recorder printed values between 660 and 788°C (1230 and 1450°F). This range corresponds to a density change of about 0.9 units on the film and a smaller density change in the prints. However, even these prints are indicative of greater changes in temperature than have been recorded in previous corrosion probe work. Such temperature excursions could account for the evidence of molten phases encountered on some probe specimens exposed in past years at the Miami County, Ohio Incinerator.

This technique can pick up local hot spots and identify temperatures accurately for regions above 760°C (1400°F). Since the emissivity of the deposits, probe samples, and thermocouple foil target were not accurately fixed, the estimated error was about 15°C (27°F). Within this precision, the thermocouple chart reading and the optical density of the foil target showed a range of less than 28°C (50°F) each during the ten minutes required to expose the four frames shown in Figure A-1. Despite the alternate bright and dark regions, the average temperature of the gas and the superheater tubes did not change appreciably. The only pronounced change was the intrusion of the combustion process into this region. This phenomenon may contribute to momentary zones of a reducing atmosphere and may also contribute to melting or softening of particulate ash.

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1. Ulrich, O. A. and McRury, P. A., "Furnace Tube Temperature Measurement by Photography", Symposium on Keeping Electric Power Plants on Steam", Battelle's Columbus Laboratories, March 1978.

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Figure A-1. Typical variations of light intensity (or temperature) in superheater zone of Harrisburg incinerator.

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APPENDIX B

PROBE SPECIMEN DATA

TABLE B-1. WEIGHT LOSS ON AIR-COOLED SPECIMENS EXPOSED TO BURNING REFUSE (WITHOUT SLUDGE)

Exposure time, hr	Alloy	Probe-sample Number	Average metal temperature, F	Average gas temperature, F	Total weight loss, g	Loss rate, mils/hr
8	A106	41-1	344	1400	0.417	0.069
		7	662		0.914	0.151
		13	835		1.356	0.224
		42-1	474	1100	0.404	0.067
		7	700		0.4380	0.072
		13	794		0.433	0.071
8	P22	41-2	427	1400	0.302	0.050
		8	695		0.676	0.111
		14	859		1.524	0.250
		42-2	535	1100	0.460	0.075
		8	720		0.540	0.089
		14	806		0.498	0.082
8	310SS	41-5	587	1400	0.15	0.025
		11	783		0.077	0.012
		17	930		0.038	0.0061
		42-5	650	1100	0.086	0.014
		11	769		0.1123	0.018
		17	836		0.079	0.013
8	347SS	41-4	544	1400	0.226	0.036
		10	755		0.110	0.018
		16	906		0.058	0.0094
		42-4	618	1100	0.098	0.016
		10	754		0.162	0.026
		16	826		0.091	0.015
8	Incoloy 825	41-6	626	1400	0.172	0.028
		12	808		0.140	0.022
		18	952		0.083	0.013
		42-6	677	1100	0.063	0.010
		12	782		0.083	0.013
		18	845		0.047	0.0075
8	Alonized Steel	41-3	491	1400	0.918	–
		9	726		0.280	–
		15	883		–	–
		42-3	580	1100	0.357	–
		9	738		0.133	–
		15	816		0.264	–

TABLE B-2. WEIGHT LOSSES ON AIR-COOLED SPECIMENS EXPOSED TO BURNING REFUSE WITH ADDED SEWAGE SLUDGE

Exposure time, hr	Alloy	Probe-sample Number	Average metal temperature, F	Average gas temperature, F	Total weight loss, g	Loss rate, mils/hr
8	A106	44-1	410	1200	0.414	0.039
		44-7	615		0.5348	0.051
		44-13	710		0.5095	0.048
8	A106	45-1	404	1500	0.3735	0.035
		45-7	624		0.8801	0.083
		45-13	788		1.1978	0.113
80	A106	43-1	350	1500	0.9866	0.0094
		43-7	703		0.9464	0.0090
		43-13	831		1.063	0.0101
816	A106	46-1	460	1500	8.733[a]	0.0081
		46-7	650		9.310[a]	0.0086
		46-13	785		7.1	0.007
8	P22	44-2	470	1200	0.4158	0.040
		44-8	635		–	–
		44-14	723		0.5677	0.054
8	P22	45-2	450	1500	0.5047	0.048
		45-8	652		0.7574	0.072
		45-14	814		1.1262	0.107
80	P22	43-2	450	1500	1.0428	0.0099
		43-8	728		1.012	0.0096
		43-14	850		1.0437	0.0099
816	P22	46-2	506	1500	8.795[a]	0.0082
		46-8	675		9.193	0.0086
		46-14	807		9.137	0.0085
8	310SS	44-5	571	1200	0.0538	0.0052
		44-11	682		0.0156	0.0015
		44-17	760		0.0359	0.0035
8	310SS	45-5	561	1500	0.2462	0.024
		45-11	734		0.2162	0.021
		45-17	890		0.0702	0.0068
80	310SS	43-5	635	1500	0.0039	Nil
		43-11	793		0.0602	0.00058
		43-17	900		0.0604	0.00059

TABLE B-2. (Continued)

Exposure time, hr	Alloy	Probe-sample Number	Average metal temperature, F	Average gas temperature, F	Total weight loss, g	Loss rate, mils/hr
816	310SS	45-5	603	1500	1.187[a]	0.0011
		46-11	742		1.168	0.0011
		46-17	873		1.801	0.0017
8	347SS	44-4	544	1200	0.0850	0.0083
		44-10	667		0.1002	0.0098
		44-16	746		0.2037	0.0198
8	347SS	45-4	521	1500	0.3687	0.036
		45-10	708		0.2225	0.022
		45-16	865		0.1113	0.011
80	347SS	43-4	590	1500	0.0450	0.00044
		43-10	775		0.1874	0.0018
		43-16	884		0.1657	0.0016
816	347SS	46-4	572	1500	2.980[a]	0.0028
		46-10	720		1.654	0.0016
		46-16	852		3.403	0.0023
8	Incoloy 825	44-6	595	1200	0.0046	0.00045
		44-12	696		0.0157	0.0015
		44-18	770		0.0222	0.0022
8	Incoloy 825	45-6	594	1500	0.0843	0.0082
		45-12	761		0.1668	0.016
		45-18	915		0.1248	0.012
80	Incoloy 825	43-6	674	1500	0.0045	Nil
		43-12	813		0.0424	0.00041
		43-18	916		0.1027	0.00100
816	Incoloy 825	46-6	626	1500	1.146[a]	0.0011
		46-12	765		1.312	0.0013
		46-18	896		2.088	0.0020

(a) Samples 46-1 through 46-7 lost protective deposits during probe removal following the fire. Their losses are expected to be unusually high while those numbered 46-8 and higher are typical for undisturbed deposits.